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THE ANALYSIS OF TURPENTINE BY FRACTIONAL DISTILLATION WITH STEAM.

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CONTENTS.

	Page.
Former methods of turpentine analysis	5
Modifications introduced	5
The new method of analysis	9
Apparatus	9
Operation	11
Results	13
Turpentine No. 19—A gum turpentine	13
Turpentine No. 14—A crude steam turpentine	16
Turpentine No. 27—A refined steam turpentine	19
Turpentine No. 22—A crude destructive-distillation turpentine	25
Conclusions	27

ILLUSTRATIONS.

	Page.
FIG. 1. Percentage weight—steam temperature curve for a mixture of two oils distilled in the ordinary manner	7
2. Percentage weight—steam temperature curve for a mixture of two oils distilled through a dephlegmator	8
3. Percentage weight—steam temperature curve for a nearly pure oil mixed with small quantities of higher boiling substances distilled through a dephlegmator	8
4. Apparatus used in turpentine analysis	9
5. Working drawing of dephlegmator	10
6. Percentage weight—specific gravity curve for a gum turpentine	14
7. Percentage weight—index of refraction curve for a gum turpentine	15
8. Percentage weight—steam temperature curve for a gum turpentine	17
9. Percentage weight—specific gravity curve for a crude steam-distillation turpentine	18
10. Percentage weight—index of refraction curve for a crude steam-distillation turpentine	20
11. Percentage weight—steam turpentine curve for a crude steam-distillation turpentine	21
12. Percentage weight—specific gravity curve for a refined steam-distillation turpentine	22
13. Percentage weight—index of refraction curve for a refined steam-distillation turpentine	23
14. Percentage weight—steam temperature curve for a refined steam-distillation turpentine	24
15. Percentage weight—specific gravity curve for a crude destructive-distillation turpentine	26
16. Percentage weight—index of refraction curve for a crude destructive-distillation turpentine	27
17. Percentage weight—steam temperature curve for a crude destructive-distillation turpentine	28

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THE ANALYSIS OF TURPENTINE BY FRACTIONAL DISTILLATION WITH STEAM.

FORMER METHODS OF TURPENTINE ANALYSIS.

In the course of the studies by the Forest Service concerning the utilization of waste yellow pine wood by distillation processes,[a] it was found that the "wood turpentines" produced by these methods were extremely variable in composition and properties, and that an accurate method for comparing and grading them was very necessary for the further progress of the work. Most of the methods of turpentine analysis in use were devised simply to detect adulterations in gum turpentine, and there was no satisfactory method applicable to all classes of turpentines which would give an accurate idea of their relative compositions and characteristics. Fractional distillation with subsequent examination of the individual fractions appeared the best for this purpose, but some modifications seemed advisable. This general method is ordinarily carried on as follows: The liquid to be distilled is heated in a flask, the vapors are condensed, and the distillate is collected in several portions or fractions; the temperatures between which the various fractions distill are recorded, and sometimes one or more physical properties of the fractions are determined. In this manner a general idea of the composition of a turpentine can be obtained, but, as will be shown later, the completeness of the separation, the ease of interpretation of the results, and the reliability of the data can be increased by extending and modifying the ordinary method.

MODIFICATIONS INTRODUCED.

The four following important changes were made:

(1) A new still head was introduced.

(2) Steam distillation was used instead of the ordinary distillation with direct heat.

(3) The graphical method of expressing results was employed.

(4) More physical properties were determined.

These changes will be discussed in order.

(1) If a mixture of two liquids with different boiling points be distilled, each of the first fractions will contain a larger proportion of the

[a] Forest Service Circular 114, "Wood Distillation."

lower boiling liquid, and each of the last a larger proportion of the higher boiling liquid; all the fractions will contain both liquids in varying proportions, and it will be impossible to separate the two liquids completely by one such distillation. By repeated distillations of the several fractions, however, and by combination of those fractions which distill between the same temperatures, a fairly complete separation can eventually be made. This is usually a long and tedious operation and not readily applicable to an analytical method.

By taking advantage of the well-known principle of dephlegmation these difficulties are largely removed and in many cases one operation will suffice to separate two liquids in practically pure condition. This principle is applied by placing between the distilling flask and the condenser a new form of column still head or dephlegmator (fig. 4). This is of such construction that the vapors are partly condensed before they reach the condenser, and the uprising vapors are therefore washed by the reflowing liquid. When a mixture of light and heavy[a] oils, such as might occur in turpentines, is distilled through this apparatus, the tendency is for the vapors of the light oil to pass freely out into the condenser, while the vapors of the heavy oil are condensed and return to the still, to be carried over only after all the light oil has been distilled. The results are the same as though repeated distillations were made.

(2) When distilling high boiling oils over a direct flame, it is difficult to regulate the temperature, and there is always danger of superheating. It is true that this superheating may be slight when the distillation is carefully carried on, but if the operation is hastened the danger may be greatly increased. In the case of turpentine and other liquids which contain unstable substances, like terpenes, superheating may cause decomposition or alteration of the oil, and for this reason a study of the properties of the distillate may not clearly show the composition of the original oil.

Not only does superheating tend to cause decomposition of the turpentine, but it introduces errors in temperature readings. Further, the rate of distillation may not be constant. These several sources of error involved in an analysis by ordinary direct heat distillation can be largely eliminated by distillation with steam, since the process can be carried on at a much lower temperature and with a more certain regulation.

The fundamental principles of distillation with steam may be outlined as follows: If a pure liquid, such as benzine, which does not dissolve in water be placed in a flask and water added, the two will upon

[a] "Light" and "heavy" are terms used synonymously with low boiling and high boiling. The terms arise from light and heavy weight—that is, low and high specific gravity which usually accompany low and high boiling points respectively.

the application of heat distill together in a fixed proportion, and the boiling point will remain unchanged as long as the two constituents of the mixture are present. This boiling will take place at a temperature below the boiling point of either the oil or the water. This lowering of boiling point is characteristic of a mixture of two mutually insoluble liquids, and because of this fact an oil with a high boiling point may be distilled with water at a temperature below the boiling point of the latter. The same conditions exist and the same results follow when saturated steam is blown into the oil. In practice the steam distillation is carried on either by mixing the water with the oil in the still and heating the still externally from beneath, or by blowing steam into the oil from a boiler; the latter process is easier to regulate.

If, however, nearly equal quantities of two oils which are freely miscible with one another and have different boiling points be mixed and distilled with steam, the proportion of oil and water constantly changes and the distillation temperature of such a mixture does not remain constant, but will vary between the approximate temperature at which the separate oils distill with steam.

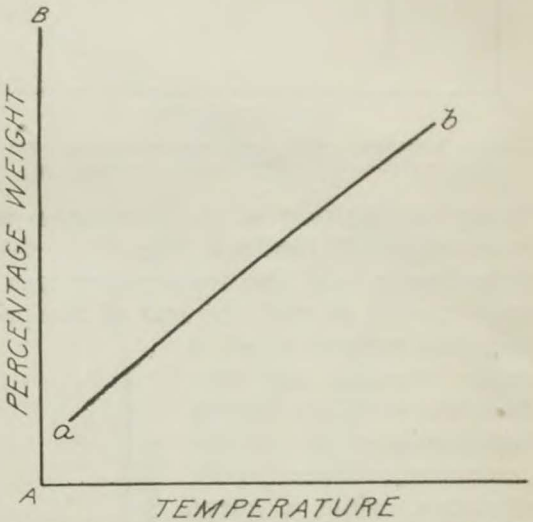

FIG. 1.—Percentage weight-steam temperature curve for a mixture of two oils distilled in the ordinary manner.

The separation of light and heavy oils by steam distillation offers the same difficulties as were mentioned in the discussion of direct heat fractionation. To remove these difficulties the principles of dephlegmation can be applied to steam distillation in the same manner as to ordinary distillation, but the still head must be of special construction.

(3) In scientific work of this character it is often very difficult, even with the data in hand, to interpret the results quickly and accurately. This is due in part to the fact that the eye can not readily grasp the meaning of a mass of figures. They are too detailed, and too much calculation is necessary in order to make comparisons. Something less complicated would greatly aid matters; a picture, as it were, which represents the exact conditions.

If in the case of an ordinary distillation without a well made still head the maximum boiling points of the various fractions be plotted on the horizontal axis, and the corresponding percentages by weight of distillate on the vertical axis, a curve which approximates figure 1 will

be obtained, which shows graphically what has happened during distillation. This curve shows that with the increase in the total percentage of oil distilled, the boiling temperature gradually rose, indicating that the proportion of the higher boiling oil increased in the later fractions. It also shows that the two oils are mixed in the various fractions in varying proportions.

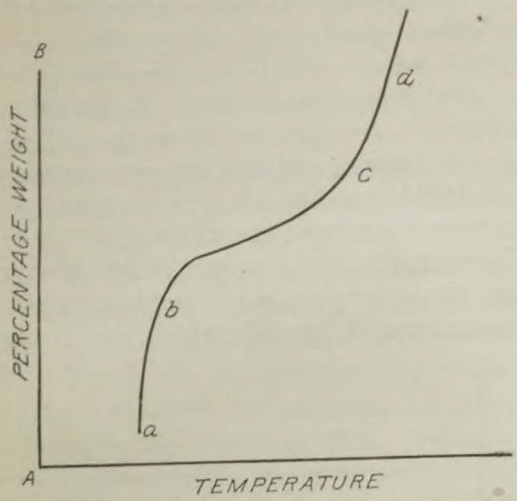

FIG. 2.—Percentage weight-steam temperature curve for a mixture of two oils distilled through a dephlegmator.

If, however, the same mixture is distilled through a dephlegmator, the percentage weight-boiling temperature curve will take a form similar to that shown in figure 2. In this figure the curve shows that during the first part of the distillation from *a* to *b* the temperature remained nearly constant, from *b* to *c* the temperature rose rapidly, while from *c* to *d* the temperature was again practically constant and remained so until the end of the process. It is evident, therefore, that a curve which is nearly vertical indicates that the distillate during that portion of the distillation consists of a nearly pure substance, while a curve which rises slowly toward the right or is nearly horizontal indicates that the distillate is composed of two or more substances. A comparison of figure 1 with figure 2 shows clearly the more complete fractionation due to dephlegmation, and also shows that when dephlegmation is used the shape of the curve gives a more accurate picture of the composition of the mixture distilled.

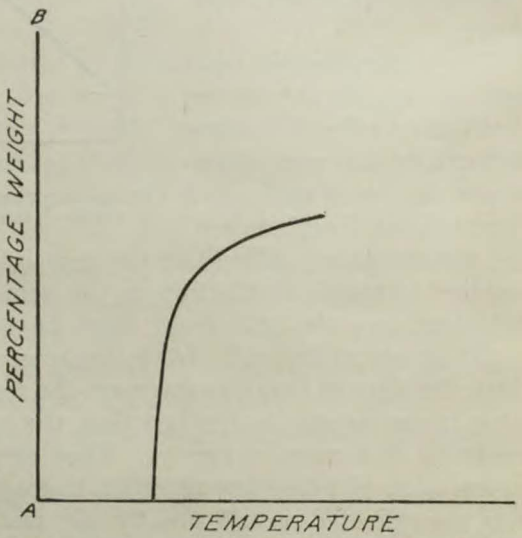

FIG. 3.—Percentage weight-steam temperature curve for a nearly pure oil mixed with small quantities of higher boiling substances distilled through a dephlegmator.

Figure 3 is the type of curve obtained when the oil distilled consists chiefly of one substance with a relatively small admixture of higher boiling substances.

(4) Any physical property, such as specific gravity or index of refraction, may be used in the place of boiling temperature in these curves; and the more physical properties determined, the greater will be the reliability of the final interpretation. In the analyses made by the Forest Service, the color, odor, and maximum boiling temperature of all fractions were noticed, and specific gravity and index of refraction were determined.

THE NEW METHOD OF ANALYSIS.

The complete method as finally modified consists, then, in distilling the sample with steam through a dephlegmator and collecting the distillate in several fractions. The color, odor, and boiling temperature of each of these fractions are noted, and the weight, specific gravity, and index of refraction of each determined. From these data, tables are made and curves are plotted. The interpretation and comparison of the curves furnish information concerning the composition of the samples as shown by the physical properties of the leading constituents, and also render the similarity or dissimilarity of various oils quickly evident.

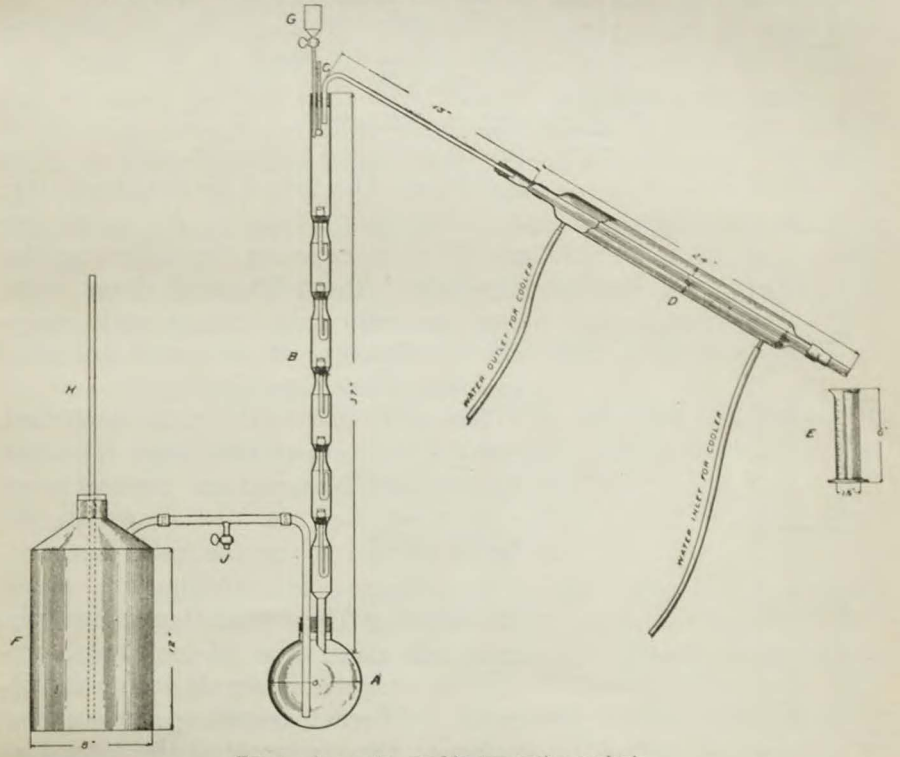

FIG. 4.—Apparatus used in turpentine analysis.

APPARATUS.

The apparatus, shown in figure 4, is supported by the ordinary laboratory stands and clamps, which are omitted in the drawing. *A*

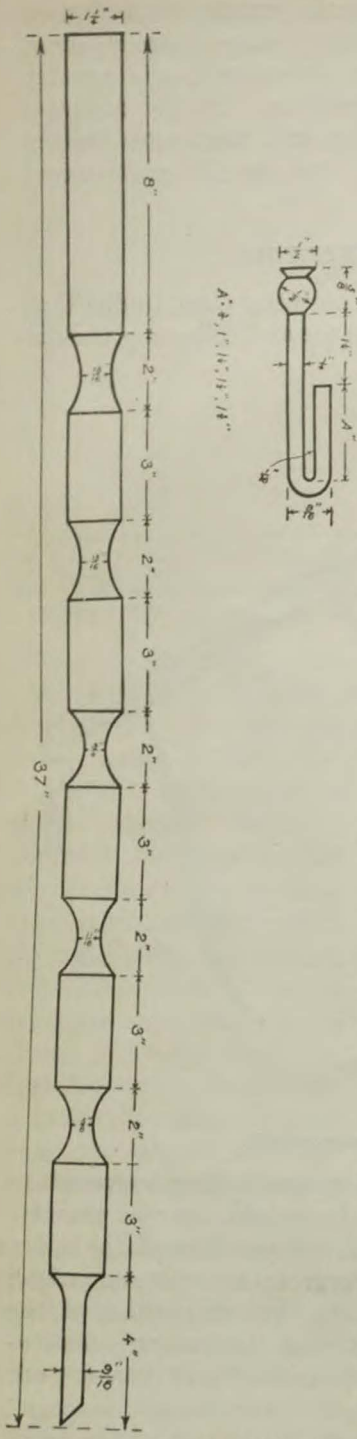

FIG. 5.—Working drawing of dephlegmator.

[Cir. 152]

is the flask which holds the turpentine to be analyzed. It is supported in a manner to permit its removal without disturbing the rest of the apparatus. *F* is the steam boiler, which is provided with a glass safety tube *H*, and in which the steam for the distillation is generated. The delivery tube through which the steam is conveyed passes through the cork at the mouth of the flask *A* and extends nearly to the bottom.

The temperature of the escaping vapors is read by means of the thermometer *C*, which is graduated to tenths of a degree centigrade. *G* is a separatory funnel arranged to permit water to drop slowly into the top of the dephlegmator, *B*. *D* is the condenser. *E* is a cylinder of 100 c. c. capacity for collecting the distillate. About fifteen of these cylinders are ordinarily used in each analysis. Ordinary cork stoppers are used to make the connections.

The still head is the most important part of the apparatus, since here the fractionation is carried on. Several forms were tried, but the one shown in the figure proved to be the most satisfactory. Figure 5 is a working drawing of the device. The foundation is an ordinary soft glass tube, 1¼-inch bore, provided at regular intervals with constrictions of different diameters, the smallest being at the bottom and the largest at the top. Traps were made by inserting into these constrictions small glass U tubes of different lengths and supporting them by brass wire-gauze collars. These tubes are inserted in order to facilitate the reflow of the condensed vapors to the flask below. They are made in the form of traps so that the uprising vapors will be forced through the meshes and between the coils of the gauze col-

lars instead of through the tube itself. The bulbs at the upper ends of the U tubes prevent them from falling, and the bends are made in order to hold a small amount of liquid, and thus act as a trap to prevent the escape of vapors through the tubes instead of through the gauze. Each trap was one-fourth inch shorter than the one below it, since it was found advisable to have successively heavier water seals from top to bottom. Each constriction was made smaller than the one above it, with the exception of the two at the top, in order to allow the collars to be easily placed in position when the dephlegmator is being constructed. A strip of 40-mesh brass gauze[a] three-eighths of an inch wide was carefully wrapped about each tube until the size of the collar was sufficient to fit its particular constriction snugly. The U was then dropped carefully into the large tube and gently forced into position with a glass rod. A snug but not tight fit is desired to prevent the tubes from blowing out of position while the apparatus is in operation and at the same time to permit of easy withdrawal for cleaning. To facilitate removal, a loop of copper wire is fastened to the top of the tube into which a hook can be inserted. In this way each section can be readily removed. It is a matter of some skill to set up the dephlegmator, but when the apparatus is once in position it is ready for a long series of determinations. Cleaning, in the case of turpentine distillations, can be done by ordinary solvents, such as alcohol and ether, without taking the apparatus apart.

Before use each time it is necessary to see that the bent tubes inside the dephlegmator are filled with water. This is done by pouring water into the top and allowing it slowly to run out.

OPERATION.

The operation of the apparatus is simple. The boiler is about half filled with water, and the separatory funnel *G* is entirely filled. The flask *A*, previously dried and weighed, is placed on a balance capable of weighing accurately to 10 mg., and exactly 500 grams of the sample of turpentine is poured in. The flask is then replaced in the position shown in the diagram. A sample of the original oil should be reserved for comparison with the several fractions of the distillate. The burner under the boiler is then lighted, and when the steam is freely escaping through the valve *J*, the valve is closed to allow the vapor to pass into *A* and the burner turned down to a point determined by experience. It is necessary to have the distillation carried on at a slow and uniform rate. Two drops of distillate per second is the rate that has been found to give the best results. In order to keep this rate constant all heat conditions must be carefully regulated. The flame under *A* should be small and low to prevent excessive con-

[a] Platinum could, of course, be used to distill liquids that would attack brass.

densation, and the burners should be surrounded by asbestos shields to keep off drafts of air. The water in *G* also is allowed to drip slowly, at the rate of about one drop per second, to insure plenty of liquid on the brass collars.

At the beginning of the distillation it is necessary to watch the still rather carefully and occasionally to relieve the steam pressure through the valve *J*, until the dephlegmator is evenly heated and the rate of reflow uniform in each section.

It is customary, in ordinary fractional distillation, to change the receiver at regular temperature intervals, which have been previously determined. In this method, however, the receiver is not changed according to prescribed temperature intervals, but according to the nature of the distillation. If the oil contains a large proportion of one substance, the temperature will remain nearly constant while that portion of the oil is being distilled. During this part of the distillation but few fractions need be taken. When, however, the oil is complex and the thermometer is rising rather rapidly, it is better to take more frequent and smaller fractions. Each time the cylinders are changed the temperature is recorded. Usually from ten to fifteen fractions are collected during one distillation. The cylinder with its contents is weighed and the weight of the dry cylinder subtracted. This gives the weight of the total distillate, which consists of both oil and water. Since by this method no greater accuracy than to 10 mg. is essential, the volume of the water in cubic centimeters as read on the cylinder can be assumed to be numerically equal to the weight of the water in grams. Subtracting this from the weight of the total distillate gives the weight of the turpentine in the fraction. By such a procedure results are obtained from which a table can be made giving for each fraction the steam temperature and the weight of oil it contains.

The odor and color of each fraction are observed and recorded at once. The specific gravity is determined, according to accepted methods, with a 10 c. c. pycnometer. The determinations are made at ordinary temperatures and corrected to give the value at 15° C. If the temperature at which the determinations are made is above 15°, then the correction factor 0.00083 is added for every degree of difference. If the temperature at which the determinations are made is below 15°, then 0.00083 is subtracted for every degree of difference. This correction factor was obtained experimentally by using a very pure wood turpentine. The index of refraction is read by means of an Abbe refractometer compensated to the D line of the spectrum, and the values corrected to 15° C. by means of factors. The factor 0.00049 is applied to all observed values below 1.4750, and is added for each additional degree of temperature above 15° C. and subtracted for each below. For oils having an index of refraction above 1.4750 the correction factor 0.00044 is similarly used. These values were

determined on two pure fractions of wood turpentine with indices of refraction above and below 1.4750, respectively.

There is now for each fraction the steam temperature, the weight, color, odor, specific gravity, and index of refraction.

RESULTS.

The results of the analyses of four different turpentines are given in the accompanying tables and curves. In the tables the data at the top show the properties of the original sample; the first column gives the serial number of the fraction; the second, the steam temperature after correction for barometric fluctuations; the third, the weight of the turpentine in each fraction. The fourth column is made by adding the weight of each turpentine fraction to the weight of all the preceding turpentine fractions, which gives the total weight of oil distilled up to each point. Thus in Table 1 up to and including fraction 3, the total weight of turpentine distilled was 267.66 grams. After all the fractions had been collected, the total weight distilled was 493.85 grams, and the undistilled residue amounted to the difference between the original weight taken, 500 grams, and the total weight distilled, 493.85 grams, or 6.15 grams. For purposes of reference and calculation it is more convenient to deal with percentage weight than with total weight, and hence the fifth column is prepared from the fourth by finding the percentages which each total weight is of the original sample. The sixth and seventh columns give the corrected values for the specific gravity and index of refraction of each fraction. From these data three curves are drawn, showing the variation of steam temperature, specific gravity, and index of refraction, respectively, with the percentage weight of the distillate.

Turpentine No. 19—A Gum Turpentine.

Table 1 and figures 6, 7, and 8 give the data obtained from the analysis of a gum turpentine according to the methods which have been described.

Table 1.—*Turpentine No. 19—A gum turpentine.*

[Specific gravity, 0.8693 at 15°; index of refraction, 1.4739 at 15°; weight of sample, 500 grams.]

No. of fraction.	Steam temperature corrected.	Weight of turpentine in fraction.	Total weight.	Percentage weight.	Specific gravity at 15° C.	Index of refraction at 15° C.
	° *C.*	*Grams.*	*Grams.*	*Per cent.*	*Sp. g.*	N_D
1	94.9	52.98	52.98	10.6	0.8668	1.4718
2	94.9	53.03	106.01	21.2	.8668	1.4717
3	95.0	53.02	159.03	31.8	.8670	1.4722
4	95.0	53.05	212.08	42.4	.8677	1.4724
5	95.0	55.58	267.66	53.5	.8674	1.4727
6	95.0	52.45	310.11	62.0	.8674	1.4730
7	95.2	52.35	362.46	72.5	.8675	1.4733
8	95.2	51.92	414.38	82.9	.8682	1.4740
9	95.7	49.57	463.95	92.8	.8684	1.4757
10	98.7	29.90	493.85	98.8	.8866	1.4849

The ten points indicated on the curve in figure 6 show the specific gravity of the ten fractions and the corresponding percentage weight

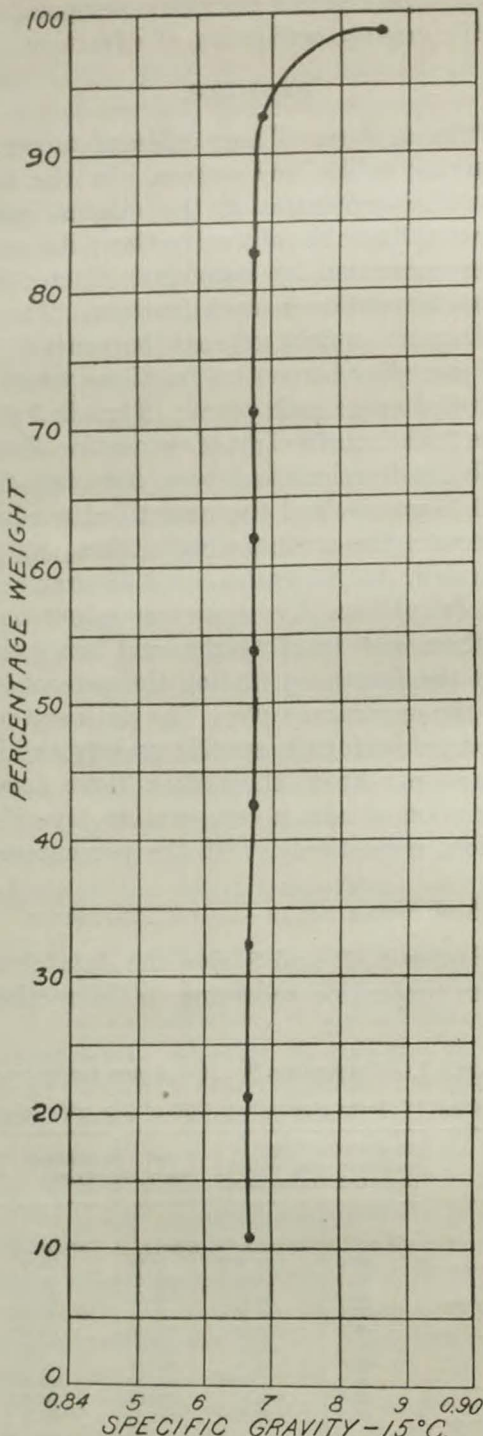

FIG. 6.—Percentage weight-specific gravity curve for a gum turpentine.

of each fraction. The specific gravity of the first 92½ per cent distilled is seen to be very uniform, as it varied only from 0.8660 to

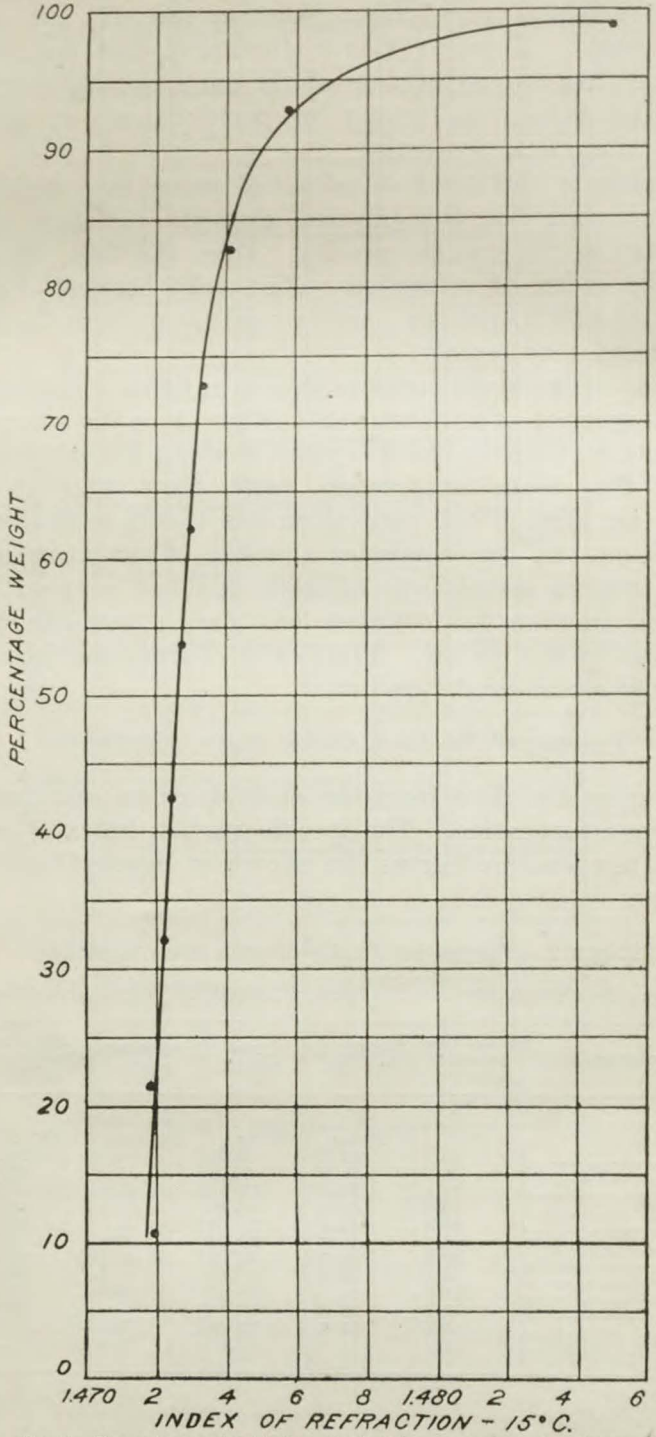

FIG. 7.—Percentage weight-index of refraction curve for a gum turpentine.

0.8685, which is .0025, or 0.29 per cent. The 6½ per cent between 92½ and 99 per cent varied widely in specific gravity, while the last 1 per cent remained undistilled. Whether this 92½ per cent was composed entirely of one substance, the curve does not decide, for it is possible that two substances of the same specific gravity were present. The term "uniformity of composition" in this paper refers only to physical properties.

On reference to the index of refraction-percentage weight curve, figure 7, it is seen that this physical property varied in about the same manner as the specific gravity. Over the first 92½ per cent distilled, the index of refraction varied only between 1.4718 and 1.4757, 0.0039, or 0.27 per cent, and beyond 92½ per cent the refractive index increased very rapidly.

The steam temperature curve as shown in figure 8 indicates about the same proportion of uniform composition, since the abrupt change in the direction of the curve takes place at about 92½ per cent. Over this range the steam temperature varies from 94.9° to 95.7° C. About 92½ per cent of this turpentine was therefore nearly uniform in composition, and the remainder consisted of a mixture of heavier oils. The original sample was colorless and had a sweet, pine-like odor. Each fraction was colorless and had a pine-like odor, and only the residue was yellow. Practically, Turpentine No. 19 would be considered a high-grade product.

Turpentine No. 14—A Crude Steam Turpentine.

Table 2 gives the data from the analysis of an unrefined, steam distilled, wood turpentine. The specific gravity, index of refraction, and steam temperature curves are shown in figures 9, 10, and 11, respectively.

Table 2.—*Turpentine No. 14—A crude steam turpentine.*

[Specific gravity, 0.8834 at 15°; index of refraction, 1.4749 at 15°; weight taken, 500 grams.]

No. of fraction.	Steam temperature corrected.	Weight of fraction.	Total weight.	Percentage weight.	Specific gravity at 15° C.	Index of refraction at 15° C.
	° *C.*	*Grams.*	*Grams.*	*Per cent.*	*Sp. g.*	*N D.*
1	95.1	32.92	32.92	6.6	0.8665	1.4701
2	95.1	51.86	84.78	18.0	.8664	1.4704
3	95.1	44.39	129.17	25.8	.8668	1.4704
4	95.2	42.64	171.81	34.3	.8666	1.4709
5	95.3	46.07	217.88	43.6	.8666	1.4709
6	95.5	45.34	263.22	52.6	.8668	1.4710
7	95.8	43.82	307.04	61.4	.8675	1.4718
8	96.1	29.02	336.06	67.2	.8685	1.4729
9	96.9	26.71	362.77	72.5	.8707	1.4744
10	97.7	22.12	384.89	77.0	.8766	1.4771
11	98.3	14.69	399.58	79.9	.8984	1.4809
12	98.7	12.41	411.99	82.4	.....	1.4852

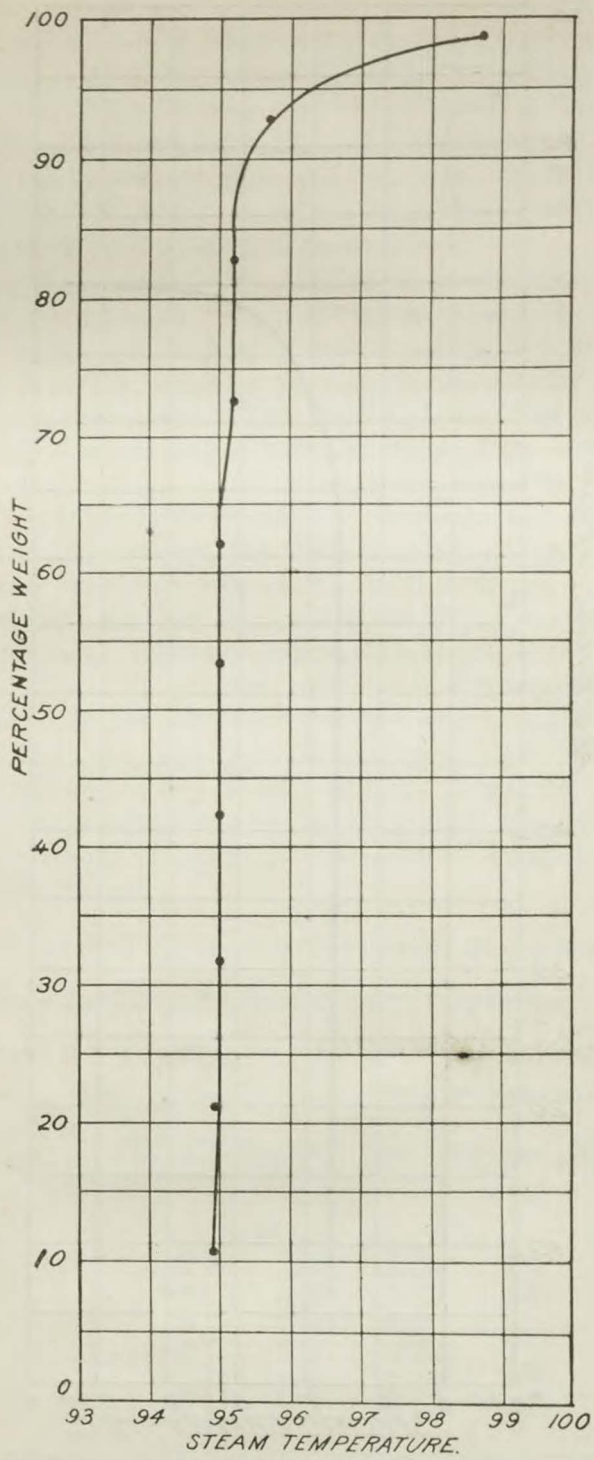

FIG. 8.—Percentage weight-steam temperature curve for a gum turpentine.

[Cir. 152]

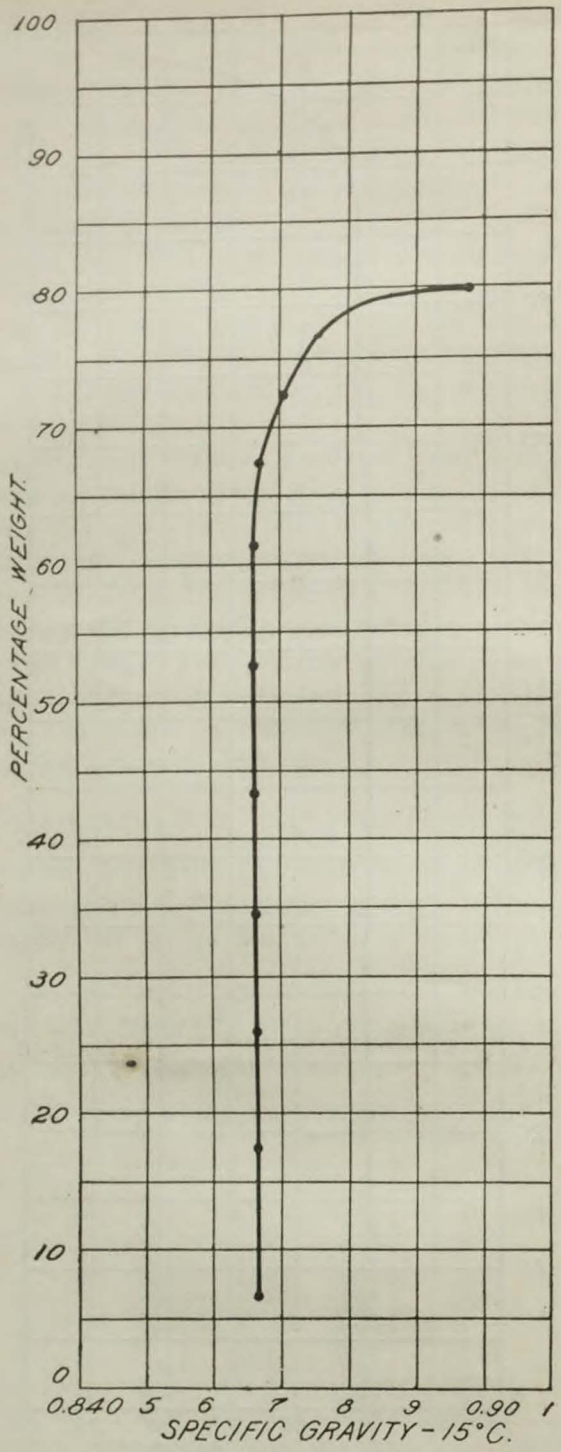

FIG. 9.—Percentage weight-specific gravity curve for a crude steam-distillation turpentine

The specific gravity curve of this turpentine, figure 9, is similar in general respects to that of the gum turpentine of Table 1. It is seen, however, that about 70 per cent of the oil has a specific gravity within a variation of 0.0025 or between 0.8665 and 0.8690, a difference of 0.29 per cent. Above this the curve turns sharply to the right and ends at 80 per cent; the balance of 20 per cent was a heavy residue which was left in the flask. It seems, therefore, from the figure that this turpentine contained 70 per cent of a pure oil.

The index of refraction curve, figure 10, confirms this conclusion. Here we find that up to 70 per cent the index of refractions varied from 1.4701 to 1.4735, a difference of 0.0034, which is 0.23 per cent, or slightly less than the variation in the specific gravity over 92½ per cent of the gum turpentine. The distillate beyond 70 per cent was of a complex character, as is shown by the shape of the curve.

The form of the steam temperature curve, figure 11, is also similar to that showing the index of refraction. It rises nearly straight at first, but turns abruptly toward the right at about 70 per cent. After combining the interpretations of the several curves, it can be concluded with safety that the oil consisted of 70 per cent of a substance of uniform physical properties mixed with about 30 per cent of complex heavier oils. The original sample was a yellowish red in color, the fractions to 70 per cent were colorless and of a pine-like but not sweet odor; from 70 to 80 per cent they were light yellow, and the residue was red and rather strong smelling. These facts lead one to believe that Turpentine No. 14 is rather poor in quality. However, by suitable methods of refining 70 per cent of a high-grade product could be made from it.

Turpentine No. 27—A Refined Steam Turpentine.

Table 3 gives the data for a refined steam turpentine.

Table 3.—*Turpentine No. 27—A refined steam turpentine.*

[Specific gravity, 0.8698 at 15°; index of refraction, 1.4709 at 15°; weight taken 500 grams.]

No. of fraction.	Steam temperature corrected.	Weight of fraction.	Total weight.	Percentage weight.	Specific gravity at 15° C.	Index of refraction at 15° C.
	° *C.*	*Grams.*	*Grams.*	*Per cent.*	*Sp. g.*	N_D
1	94.9	51.50	51.50	10.3	0.8662	1.4692
2	94.9	53.09	104.59	20.9	.8659	1.4694
3	94.9	52.75	157.34	31.5	.8659	1.4697
4	94.9	50.92	208.26	41.7	.8660	1.4697
5	95.1	58.01	266.27	53.3	.8659	1.4697
6	95.1	54.61	320.88	64.2	.8658	1.4697
7	95.1	48.35	369.23	73.9	.8660	1.4699
8	95.7	47.03	416.26	83.3	.8662	1.4707
9	96.4	44.42	460.68	92.1	.8685	1.4722
10	98.0	[a]30.00	490.68	98.1	.8756	1.4757

[a] About.

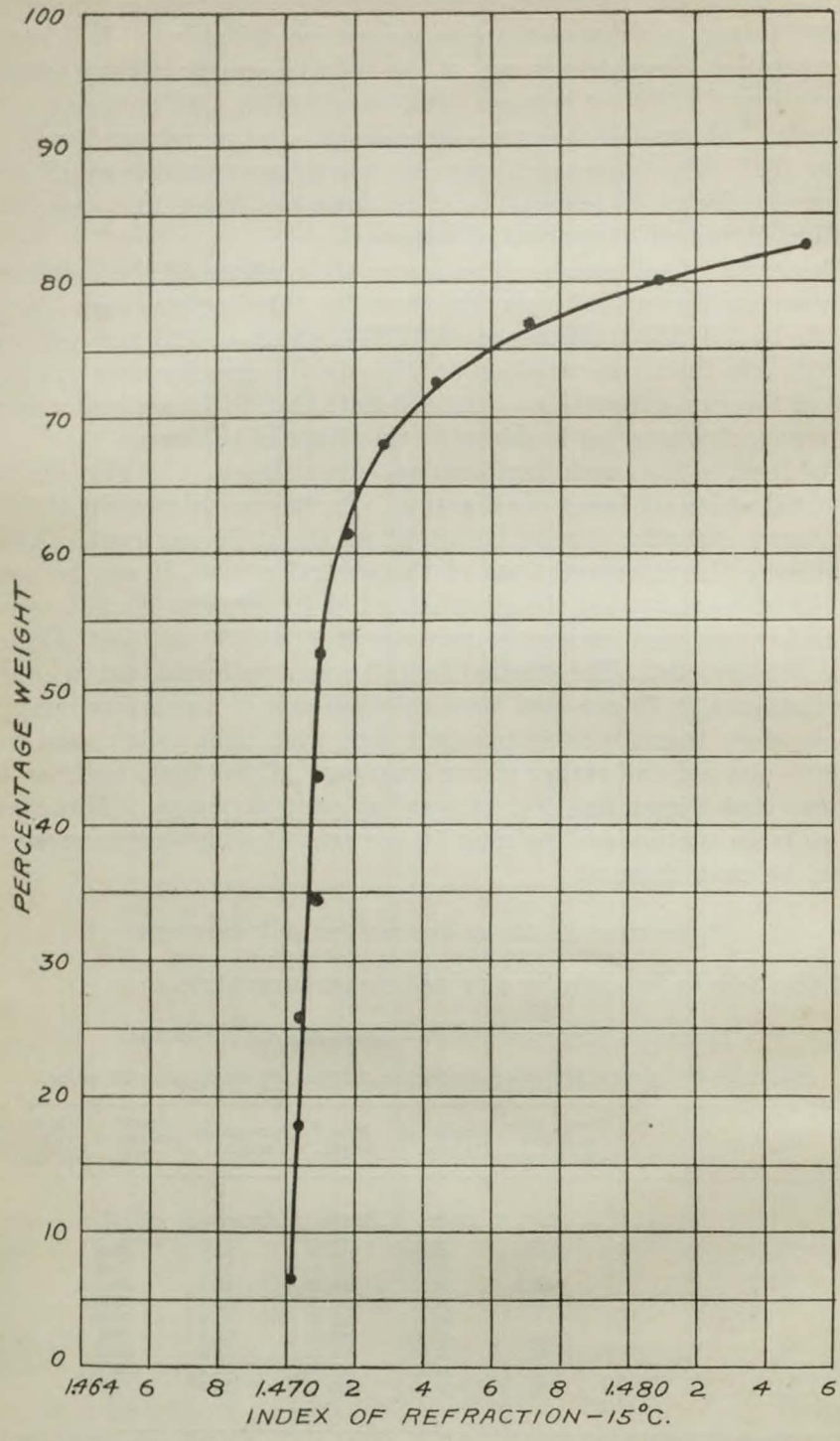

FIG. 10.—Percentage weight-index of refraction curve for a crude steam-distillation turpentine.

[Cir. 152]

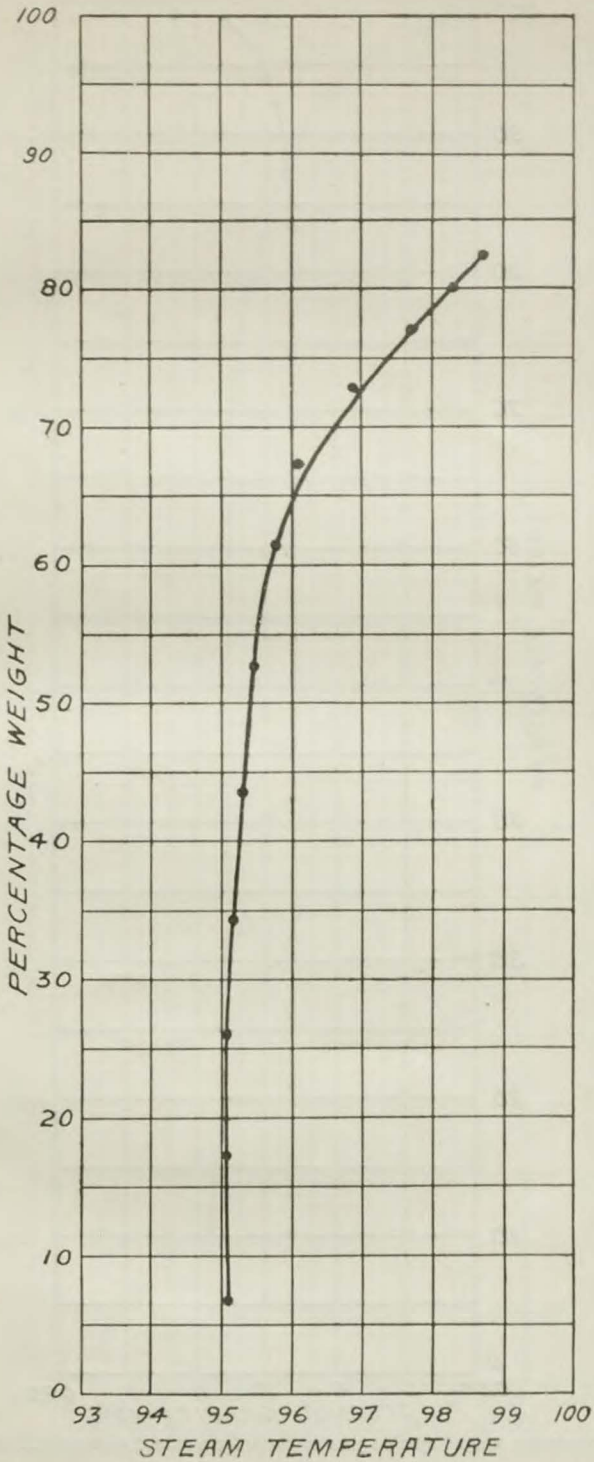

FIG. 11.—Percentage weight-steam temperature curve for a crude steam-distillation turpentine.

[Cir. 152]

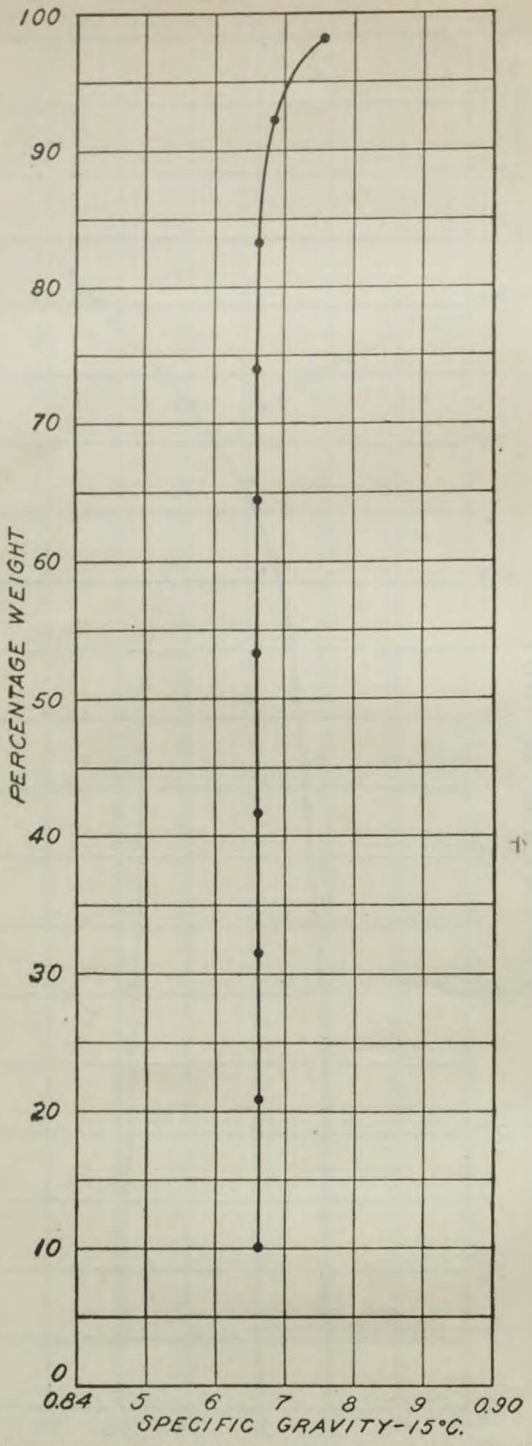

FIG. 12.—Percentage weight-specific gravity curve for a refined steam-distillation turpentine.

[Cir. 152]

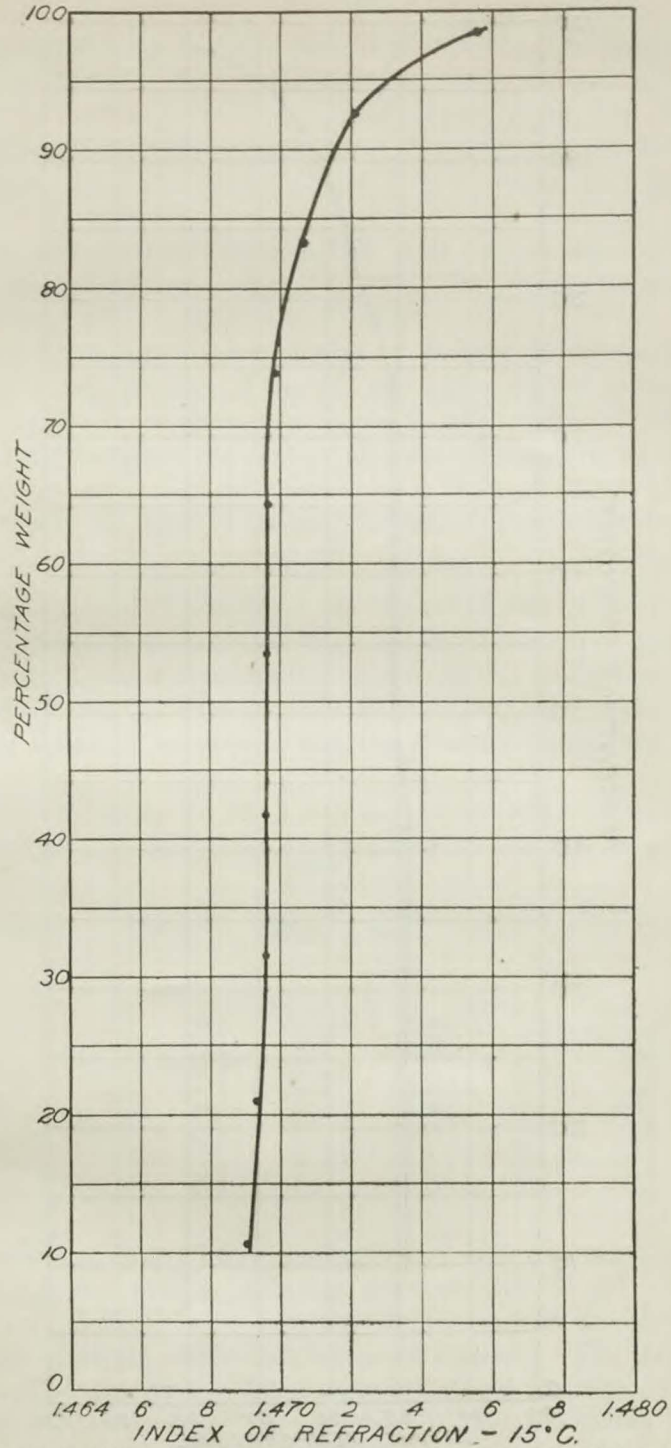

FIG. 13.—Percentage weight-index of refraction curve for a refined steam-distillation turpentine.

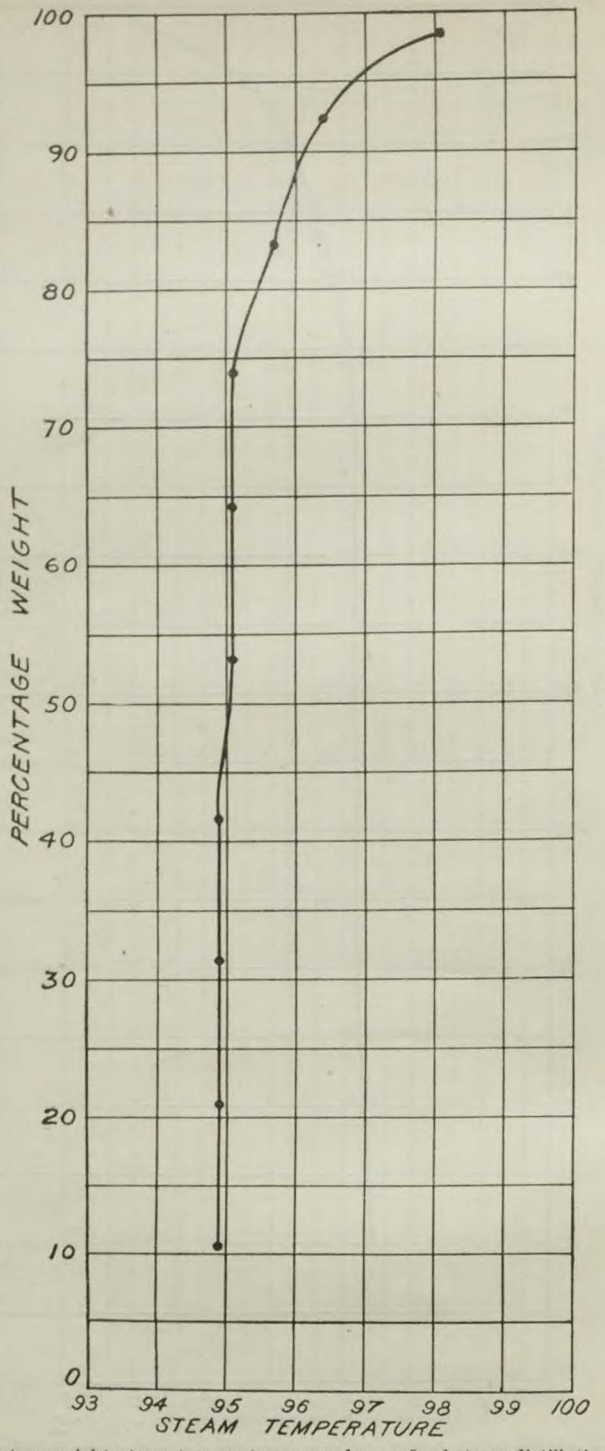

FIG. 14.—Percentage weight-steam temperature curve for a refined steam-distillation turpentine.
[Cir. 152]

The specific gravity curve is shown in figure 12. The specific gravity of the first 92 per cent of the distillate varied within the limits of 0.8662 and 0.8685. This is almost exactly the difference found in figure 1. The vertical part of the curve is very straight, and change of direction does not take place until nearly all the oil has distilled. This indicates, then, that the product was of high grade, and consisted chiefly of a pure light oil.

The index of refraction curve, figure 13, is very similar to that for the gum turpentine shown in figure 7. This change over 92 per cent is from 1.4692 to 1.4722, a difference of 0.0032.

The steam temperature curve, figure 14, further shows marked constancy over a large portion of the oil, and although not quite so perpendicular as the curve shown in figure 8, still within 1.5° variation in temperature the same per cent of oil distilled, namely, 92 per cent. The inference, then, is that this turpentine is of a high degree of purity, being practically the equal of the gum turpentine previously described.

TURPENTINE NO. 22—A CRUDE DESTRUCTIVE-DISTILLATION TURPENTINE.

The possibilities of this method are further shown in the results of an analysis of crude turpentine produced by destructive distillation of pine wood. Table 4 presents the data from this analysis. Figures 15, 16, and 17 are the curves made from this table for the specific gravity, the index of refraction, and the steam temperature, respectively.

TABLE 4.—*Turpentine No. 22—A crude destructive-distillation turpentine.*

[Specific gravity, 0.9231 at 15°; index of refraction, too dark for a determination; weight taken, 500 grams.]

No. of fraction.	Steam temperature corrected.	Weight of fraction.	Total weight.	Percentage weight.	Specific gravity at 15° C.	Index of refraction at 15° C.
	° *C.*	*Grams.*	*Grams.*	*Per cent.*	*Sp. g.*	N_D.
1	94.1	10.20	10.20	2.0	.....	1.4584
2	94.7	13.66	23.86	4.8	0.8674	1.4691
3	95.1	26.71	50.57	10.1	.8656	1.4703
4	95.3	36.03	86.60	17.3	.8644	1.4719
5	96.1	46.23	132.83	26.6	.8631	1.4737
6	96.5	42.42	175.25	35.1	.8620	1.4763
7	96.9	39.71	214.96	43.0	.8603	1.4791
8	97.6	34.02	248.98	49.8	.8628	1.4852
9	.....	24.23	273.21	54.6	.8728	1.4910
10	98.5	18.74	291.95	58.4	.8904	1.4962
11	98.7	15.33	307.28	61.5	.8933	1.4993

On reference to figure 15 the oil seems fairly uniform over 50 per cent of its composition, with a variation between 0.8678 and 0.8600, or 0.0078. The specific gravity, however, decreases with the distillation, whereas that of all the other samples has increased. This indicates a very different composition. The irregular form of the index of refraction and steam temperature curves (figs. 16 and 17) shows that the oil was one of very complex composition.

The odor, both of the sample and the fractions, was strong and disagreeable, while the color varied from a yellow to a red.

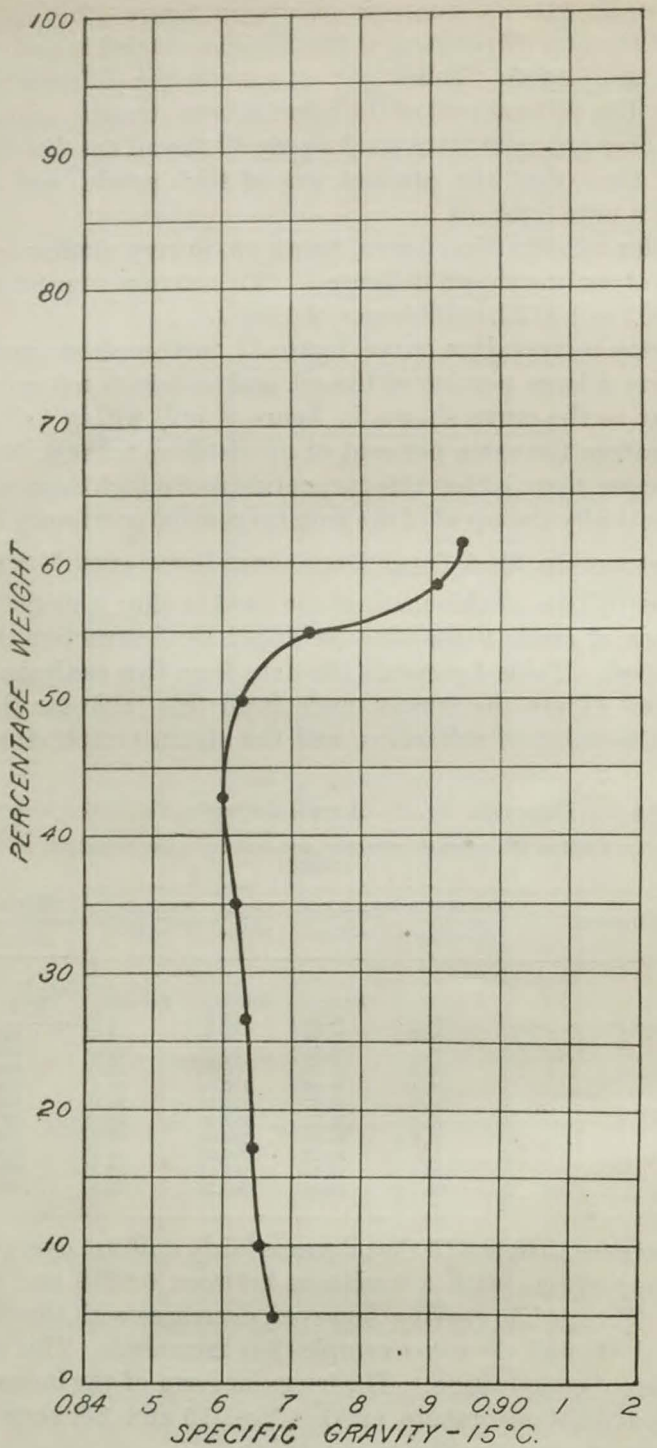

FIG. 15.—Percentage weight-specific gravity curve for a crude destructive-distillation turpentine.
[Cir. 152]

It is perfectly possible, then, to distinguish a complex oil by the irregularities in the shape of the curve, and when several oils of widely varying properties are present in any mixture this method of analysis will show their presence.

CONCLUSIONS.

This article has outlined a method of analysis by fractional distillation with steam, and has shown the results of the application of this method to four turpentines of different kinds.

In discussing the results three physical properties have been given emphasis—specific gravity, index of refraction, and temperature of

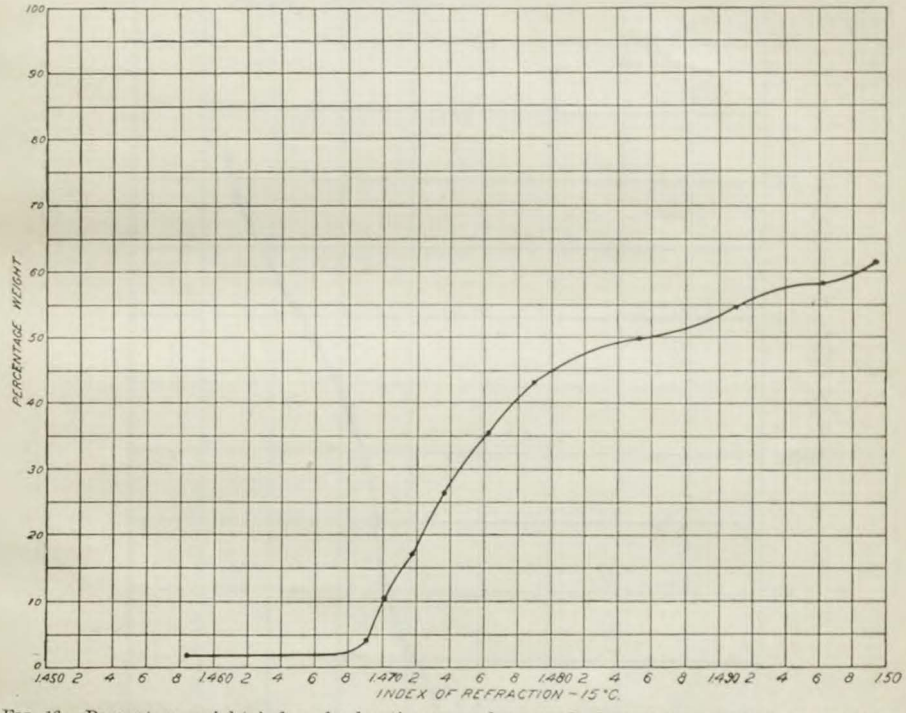

FIG. 16.—Percentage weight-index of refraction curve for a crude destructive-distillation turpentine.

distillation with steam. These three properties were chosen because they lend themselves to rapid determination and clear interpretation. The odor and color were also found to be of value in the final conclusions. The basis for the judgment of an oil has been the combined interpretations from the various physical properties as indicated in the shape of the curves, and no one physical property has been assumed to be all-conclusive. The interpretations from the various physical properties have been seen, however, to harmonize very well.

Certain advantages of this method seem worthy of mention.

(1) By introducing the principle of dephlegmation the separation of the constituents is made much more complete.

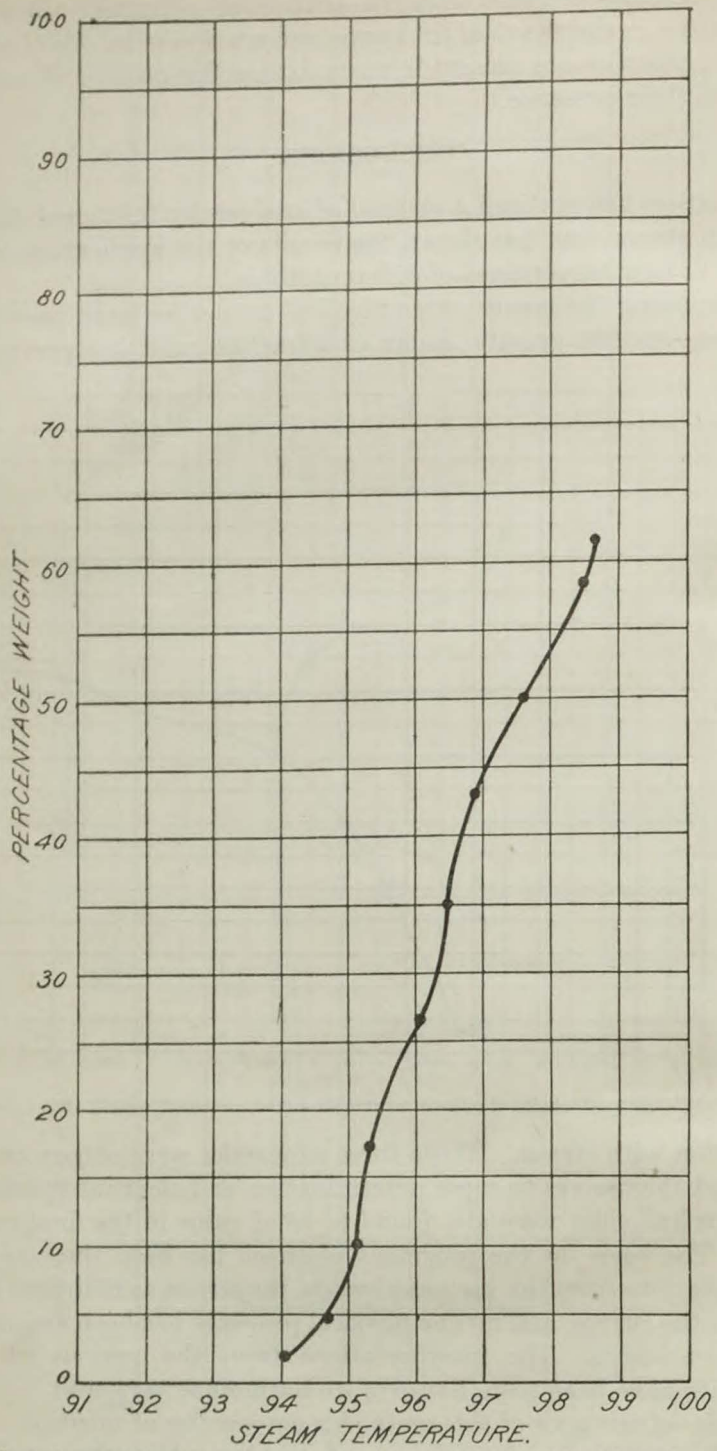

FIG. 17.—Percentage weight-steam temperature curve for a crude destructive-distillation turpentine.
[Cir. 152]

(2) The graphical method of expressing the data gives a ready means of interpreting the results and comparing various turpentines.

(3) The large amount of data obtained makes the results very reliable.

(4) The low temperature at which the distillation is carried out reduces the danger of alteration of the sample during the analysis.

(5) The distillation is similar to certain technical distilling processes which have been found to give excellent results in practice, and suggests the possible results of applying such methods to the refining of turpentines.

Approved:

JAMES WILSON, *Secretary.*

WASHINGTON, D. C., *May 8, 1908.*

[Cir. 152]

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